# CHEMISTRY OF NATURAL PRODUCTS

*Dissertation Submitted for the Award of the Degree of*

**Master of Philosophy**

IN

CHEMISTRY

BY

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DEPARTMENT OF CHEMISTRY
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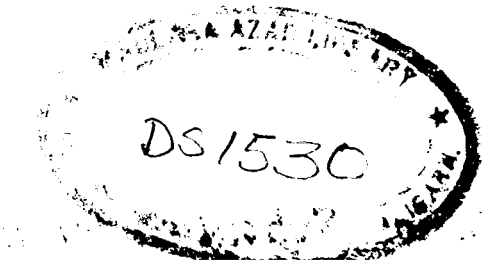
ALIGARH MUSLIM UNIVERSITY
ALIGARH

1988




DISSERTATION SUBMITTED

TO

THE DEPARTMENT OF CHEMISTRY

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IN

PARTIAL FULFILLMENT

OF THE

REQUIREMENTS FOR THE AWARD

OF THE

DEGREE OF M.Phil

IN

CHEMISTRY

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Zeba Saeed Siddiqui

( Zeba Saeed Siddiqui )

# C O N T E N T S

# I N T R O D U C T I O N

# INTRODUCTION

The work carried out in the context of this thesis involved isolation, identification and, if necessary, structural elucidation of compounds isolated from Desmodium sequax (leguminoceae). It had been earlier investigated in this laboratory but no crystalline compound could be isolated from it, though tlc showed the presence of a number of highly fluorescent compounds in the plant extract. It was therefore desired to repeat the work and attempt isolation through more exhaustive chromatography. Attempt to separate the components through preparative tlc did not succeed as the RF values of the constituents were too close. Recourse was then taken to column chromatography to effect as much resolution of the mixture as possible. This led isolation of a number of products in small amounts which were then purified through repeated crystallization. In all seven compounds were isolated in this way which were labelled as DS-1, DS-2, DS-3, DS-4, DS-5, DS-6 and DS-7.

| Sample code | m.p.°C |
|---|---|
| DS - 1 | 160 |
| DS - 2 | 156-8 |
| DS - 3 | 138-40 |
| DS - 4 | 192-200 |
| DS - 5 | 178-80 |
| DS - 6 | 204-206 |
| DS - 7 | 256-60 |

All except DS-2 turned out to be flavonoids of known structure. The structures were inferred through analysis of their nmr and mass spectra which are discussed in this thesis. The spectral characteristics of DS-2 indicate it to be either a terpene or sterol- the low melting point favouring the latter possibility. Owing to purity of material in hand- and the difficulty in collecting spectral data, its structure could not be so far elucidated.

Another plant Xanthoxylum simularis was also investigated because the member of the family rutaceae specially the genera Xanthoxylum are well known for the presence of alkaloid and coumarin. Preliminary work has so far supplied only a terpenoid. The structure of this compound which appears to be similar to limonin is also under investigation.

In the theoretical section the important features of the flavonoid spectra are reviewed briefly.

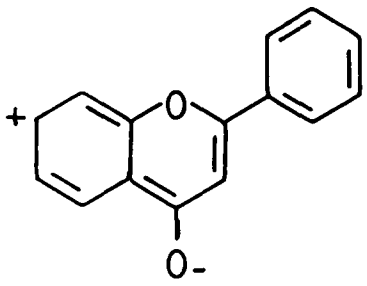
# THEORETICAL

# THEORETICAL

## The spectroscopic identification of flavonoids

### (i) Ultra Voilet

UV spectra of different flavonoids are very characteristic and along with colour reactions, have been used extensively to distinguish various groups of this class of compounds. The absorption maxima of flavones have been correlated to the presence of a cinnamoyl and a benzoyl chromophore, the former giving rise to the high wavelength band at 320–380 nm and the latter to the low wavelength band at 240–270 nm. On the basis of this generalisation important deductions have been made about the location of the substituent in the two rings.



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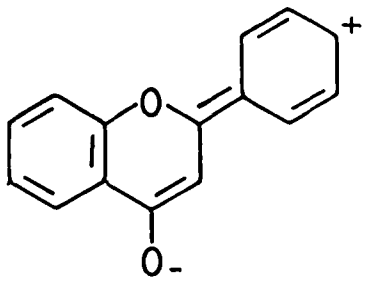

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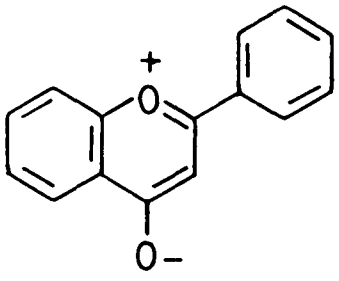
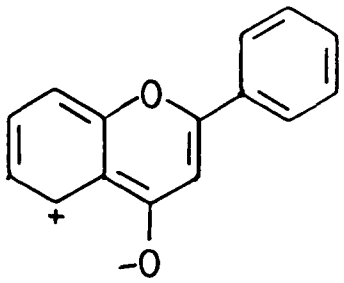


III



IV

Substitution in the B ring specially at 4' position stabilises the cinnamoyl chromophore resulting in a bathochromic shift of band I whereas substitution in the A ring has a similar effect on the position of band II. Compounds having a hydroxyl group at 5 position absorb at higher wavelength due to chelation with the carbonyl group and methylation of this hydroxyl causes a hypsochromic shift of 10–15 nm. The presence of hydroxyl at this position is established by measuring the spectrum in presence of anhydrous aluminium chloride which brings about the significant bathochromic shift of both the bands due to the formation of chelated complex. The behaviour of 3-hydroxyl group is similar to 5-hydroxyl group. Hydroxyl groups at 7 and 4' are more acidic than others due to the localization of positive charge and consequently its ionization is observed even by a weak base such as sodium acetate[1] resulting in a bathochromic shift of 8–20 nm of both the bands. In flavanones absence of cinnamoyl chromophore has the effect of suppressing the high wavelength band, which is either totally absent or present only as an inflection. In isoflavones only the benzoyl chromophore is present, the spectra are therefore, marked by the absence of high wavelength band. Thus it is difficult to distinguish between flavanones and isoflavones with the help of UV alone.

(ii) Infrared

The ir spectrum of flavone shows the carbonyl absorption at 1660 $cm^{-1}$ owing to conjugation with the olefinic

double bond. Earlier investigations in the carbonyl region were undertaken by Hergret and Kurth[2], Inglet[3] and Looker and Hanneman[4]. These authors attempted to correlate the carbonyl absorption frequencies with substitution pattern and noted the existence of both intramolecular and intermolecular hydrogen bonding. According to these authors the carbonyl frequency in flavones is independent of the substitution pattern in ring A and ring B is affected only by the introduction of a hydroxyl group at 3 position.

The ir spectrum of flavonone shows the carbonyl band at 1680 $cm^{-1}$, the standard value for aromatic ketones. The shift of the carbonyl band to 1620 $cm^{-1}$ in 5-OH flavonones is largely due to electron donation by the ortho hydroxyl group, coupled with chelation and methylation of this hydroxyl causes a small hypsochromic shift of 10 $cm^{-1}$. A similar shift towards long wavelength is observed in 4' substituted flavonone due to intermolecular hydrogen bonding. The ir spectra of isoflavones are similar to those of flavones.

(iii) Nuclear Magnetic Resonance

The nmr spectrum provides unambiguous evidence for many structural features met with in flavonoids but progress in this field was hampered at first by the sparing solubility of flavonoids in solvents normally used for measurement of nmr spectra. The derivatives of flavonoids such as methyl ether and acetates though soluble in these solvents are not

ideally suited due to interference from signals of methoxyl and acetoxyl groups, which also effect the signals of the adjoining protons. These difficulties have been overcome by the use of trimethyl silyl derivative of flavonoids by Mabry et. al[5].

Since the position of signal of the individual protons varies with the electron density at carbon atoms to which they are attached, the nmr spectra of flavonoids can be best understood by a reference to mesomeric structure described as the benzoyl and cinnamoyl chromophores in connection with UV spectroscopy. In accordance with this analogy protons at 7 and 4' positions of the flavone molecule are shifted down field compared to other protons of ring A and B. The most deshielded proton is, however, the one at C-5 which apart from its ortho relationship to the carbonyl group and the consequent electron withdrawl from it by mesomeric effect, lies in the deshielding zone of the carbonyl cone.

The A ring of flavones commonly has the phloroglucinol substitution pattern. Thus in 5,7-dihydroxy flavone the protons at C-6 and C-8 appear separately as doublets at $\delta$5.7-6.9(J = Ca 2.5 Hz). The C-6 doublet consistently appears at higher field than C-8 and methylation of 7-hydroxyl group causes both signals to shift down field. However, complications arise due to protons of ring B which normally has the catechol substitution pattern in flavones and resorcinol

substitution pattern in isoflavones. In 4' substituted flavones protons at C-2', 3', 5' and 6' due to free rotation of the ring, appear as two pairs of ortho coupled doublets at δ6.5-7.9(J = Ca 8.5 Hz) that is somewhat downfield than the A ring protons due to conjugation of B ring with the carbonyl group. In 3', 4' disubstituted flavones and flavonols C-5' proton gives rise doublet in the region δ 6.5-7.1(J = Ca 8.5 Hz) whereas C-2' and C-6' protons appear as a multiplet between δ 7.2-7.9 thus, showing AA'B coupling pattern. In 3',4',5' trisubstituted flavones the C-2' and 6' protons give a singlet of two protons.

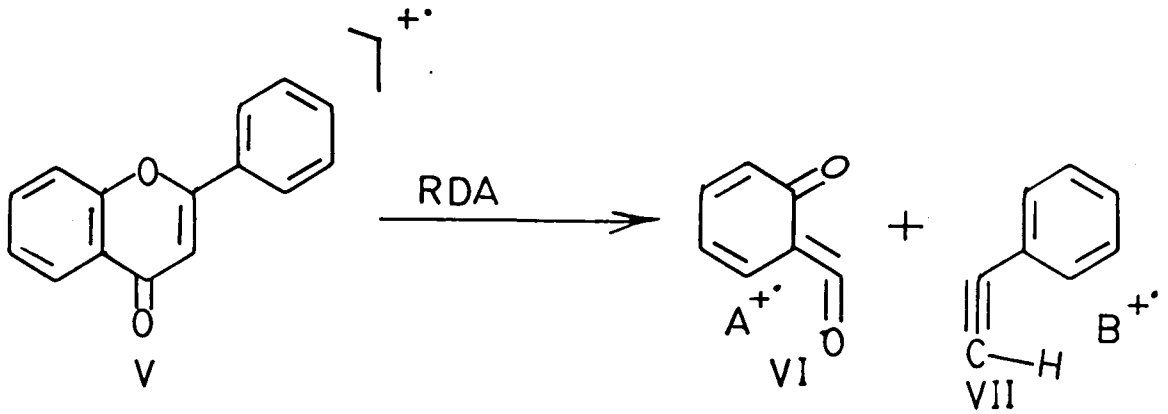
The hydroxylic protons of flavones indicate sharp signals whose chemical shifts are again characteristic of their location in the molecule. Thus, the chelated 5-hydroxyl group occurs at δ 13.0 but the presence of a hydroxyl at C-3 leads to reduced deshielding of the 5-hydroxyl which now resonates at δ 7.5. The C-3 hydroxyl itself appears at δ 9.4 while signals of 4' and 7-hydroxyl groups merge with signals of the aromatic protons.

The nmr spectra of flavones and isoflavones differ from each other most noticeably in that isoflavones show one proton singlet at δ 7.9. This arises from the proton at C-2 and is of diagnostic importance. Another feature which distinguishes the spectra of two classes of compound is that in

isoflavones protons of ring B occur at higher field compared to the protons of this ring in flavones, since in isoflavones it is not conjugated to the pyrone carbonyl.

(iv) Mass Spectrometry:

The mass spectra of oxygenated heterocycles have been the subject of detailed studies by Pelter[6], Reed[7] and Barnes[8] et. al. According to Pelter[9], the mass spectral fragmentation pattern of these compounds is sensitive to variation in the oxygenation pattern which makes it difficult to formulate a general break down pattern for different members of this class of compounds. Thus, for example, the retrodiene fragmentation of flavone (V) itself gives rise to a peak due to the species (VI) which is 80% of the molecular ion peak whereas in more oxygenated compounds its intensity is only 15–18% of the molecular ion peak.




Substitution pattern in A and B ring can be detected by examining m/z value of $A^{+\cdot}$ and $B^{+\cdot}$, for example 5,7-dihydroxy flavone[10] gives the same $B^{+\cdot}$ fragment(m/z 102) but produces $A^{+\cdot}$ ion 32 m.u. higher that is m/z 152 instead of

m/z 120, thus indicating two additional oxygen atoms in A ring. Similarly m/z value can pinpoint substitution pattern in B ring, for instant, leuteolin 3', 4'-dimethyl ether[11] gives $B^{+\cdot}$ ion at m/z 162 which clearly indicated the presence of two methyl groups in the molecule.

# D I S C U S S I O N

## DISCUSSION

Desmodium sequax grows in the Himalayan region of North India and South Nepal. The material used for the present study was collected from Nepal and a specimen of it was identified by the Botany Department of Tribhuvan University of Nepal. A survey of the literature revealed the presence of indole alkaloids, pterocarpans and some flavonoids in other species of Desmodium but the plant extract gave negative tests for alkaloids and has been shown to contain only flavonoids and some terpenes. The compounds so far identified were reported earlier from Pongamia glabra by Seshadri [12] et.al.

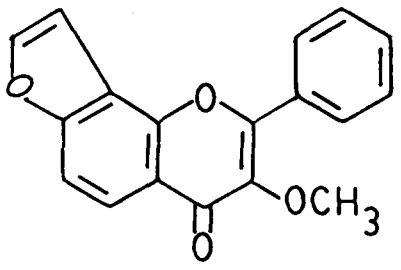
### General procedure for extraction and isolation:-

The plant material was extracted with solvents of increasing polarity. Purification was effected by column chromatography over silica gel (60-120 mesh). A number of colour reactions have been reported in literature for detecting particular structural features. The more commonly used colour reactions are Schinoda's test (Mg/HCl) for flavones and emerald green colour with gallic acid and sulfuric acid for the methylenedioxy group. Starting from larger amounts of the plant material and employing exhaustive column chromatography six crystalline compounds were isolated. These were DS-1, DS-3, DS-4, DS-5, DS-6 and DS-7.

DS-1 :

The ir spectrum (fig.1) shows pronounced absorption at 1635, 1625 and 1605 $cm^{-1}$ indicating the presence of a chromone moiety in the molecule.

The nmr spectrum (Fig.2) shows a 3H singlet of the methoxyl methyl at δ3.9. The aromatic region of the spectrum clearly establishes the presence of a benzofuran moiety by meta coupled doublets at δ7.2 and 7.83(J = 2Hz) and an ortho coupled doublet at δ8.2(J=9.5 Hz). The compound is thus identified as a furoflavanoid and the 6H multiplet between δ7.4-8.1 can be attributed to the protons of ring B and C-6 proton in the molecule. Combining these features one arrives at structure (1) for the compound which is in complete accord




(1)

with the mass spectrum (Fig.3). This shows however $M^{+\bullet}$ at m/z 291 (base peak) rather than at m/z 292, the required value. The m/z 291 peak created initially much confusion as owing to the odd value of $M^{+\bullet}$, the compound was mistaken for an alkaloid.

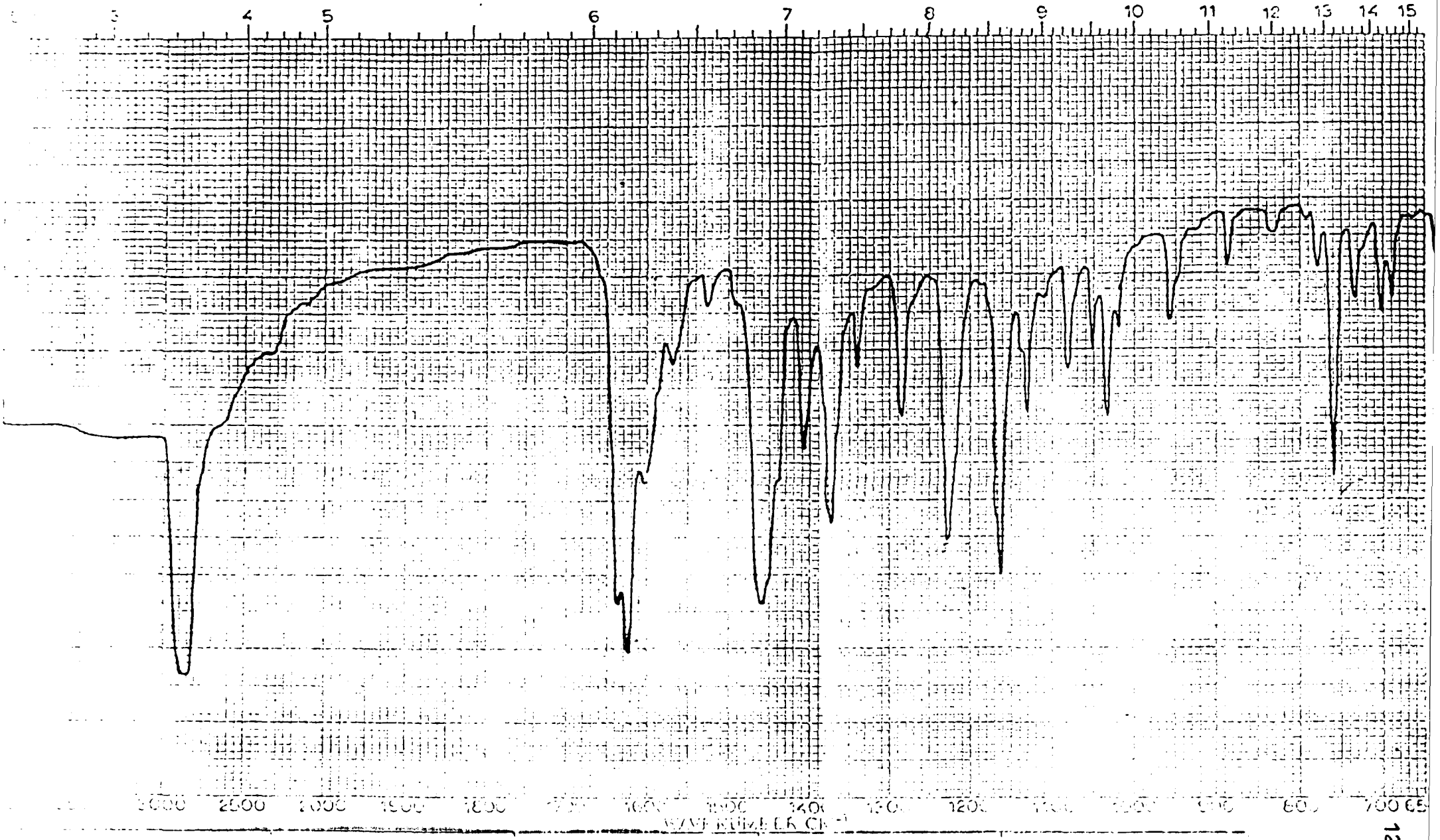

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FIG.1

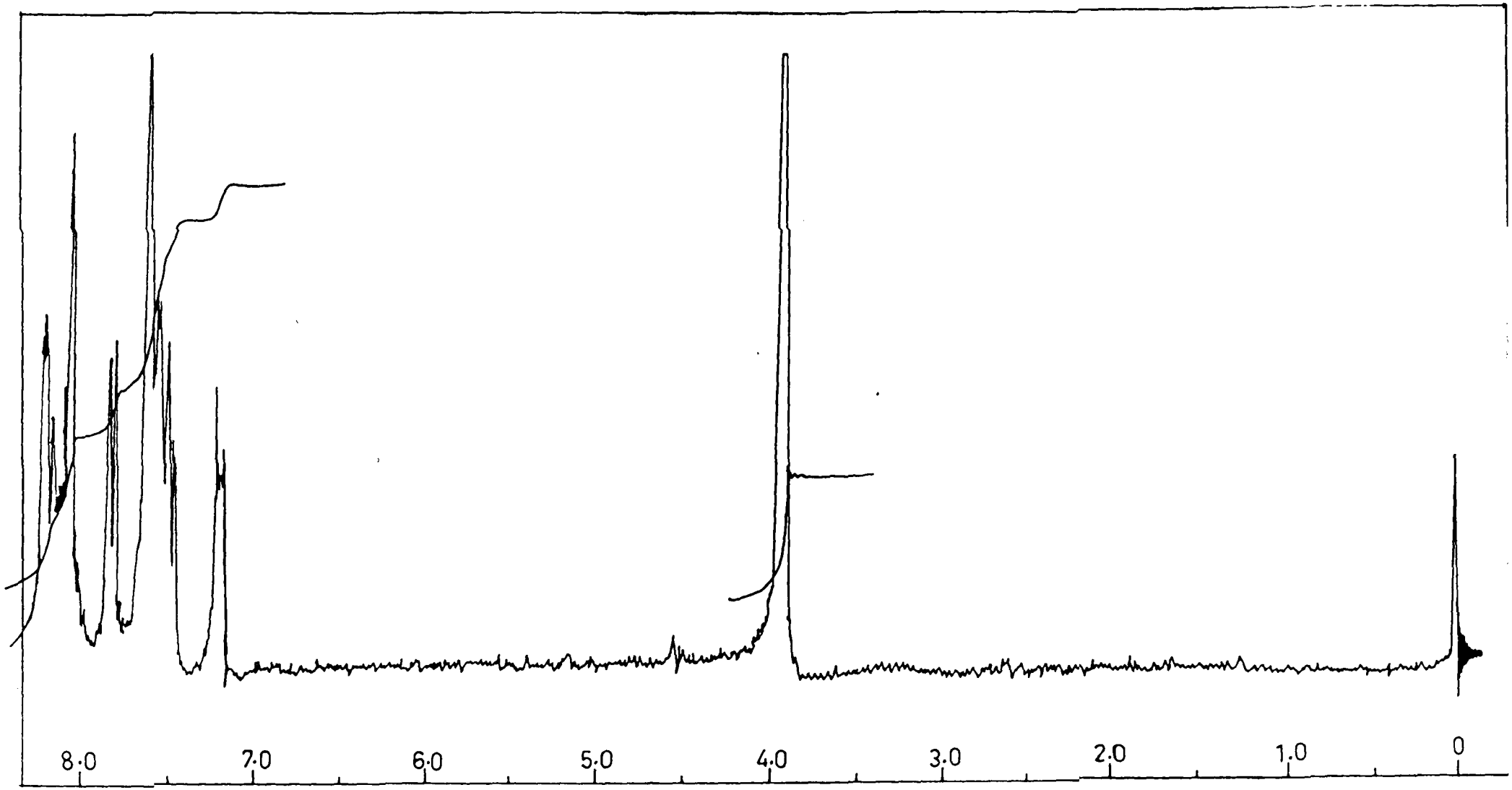
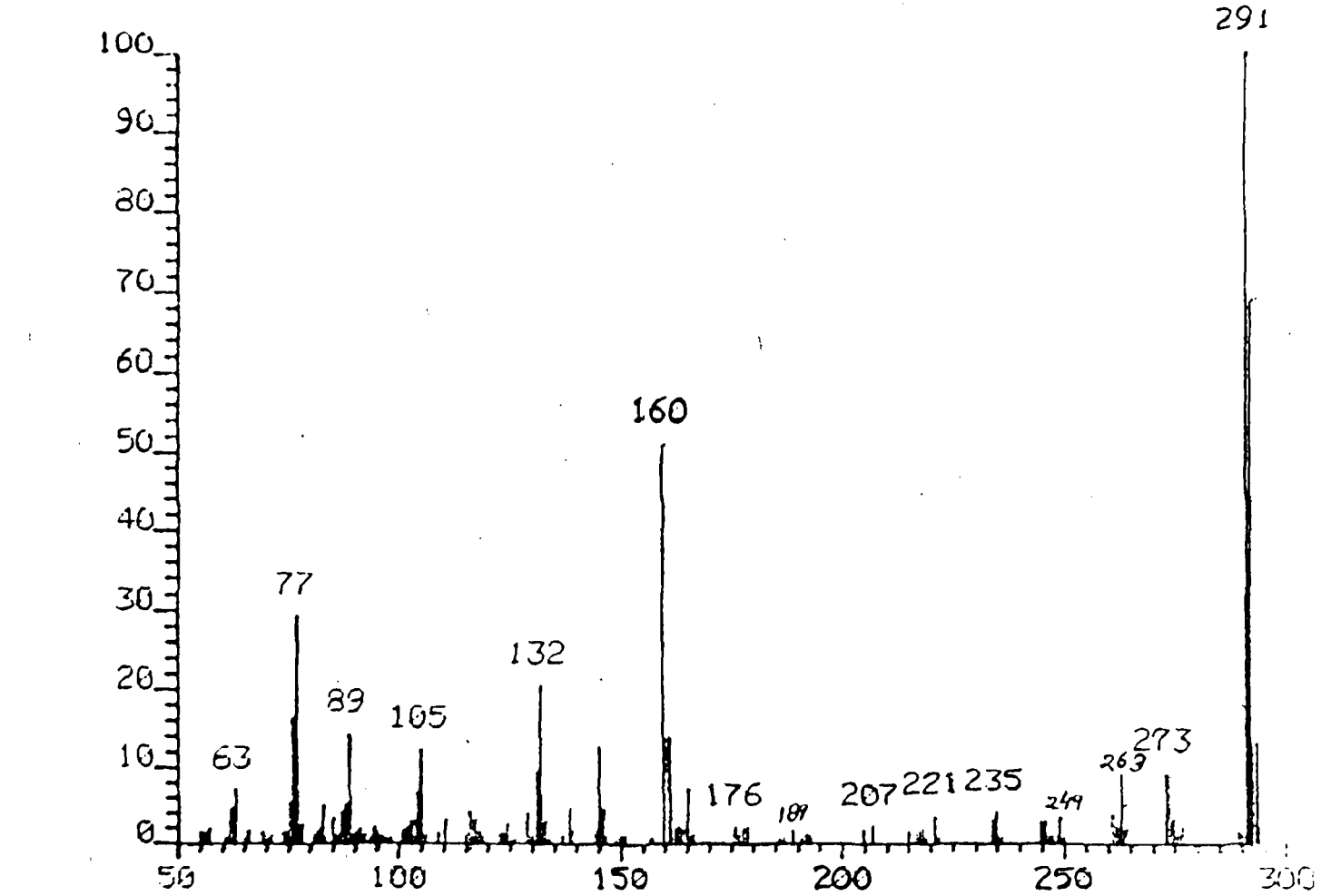



FIG.2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273
***** E.I.MASS MAT.112 E *****
ANALYSIS NAME: DS1.DAT
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NORM: E
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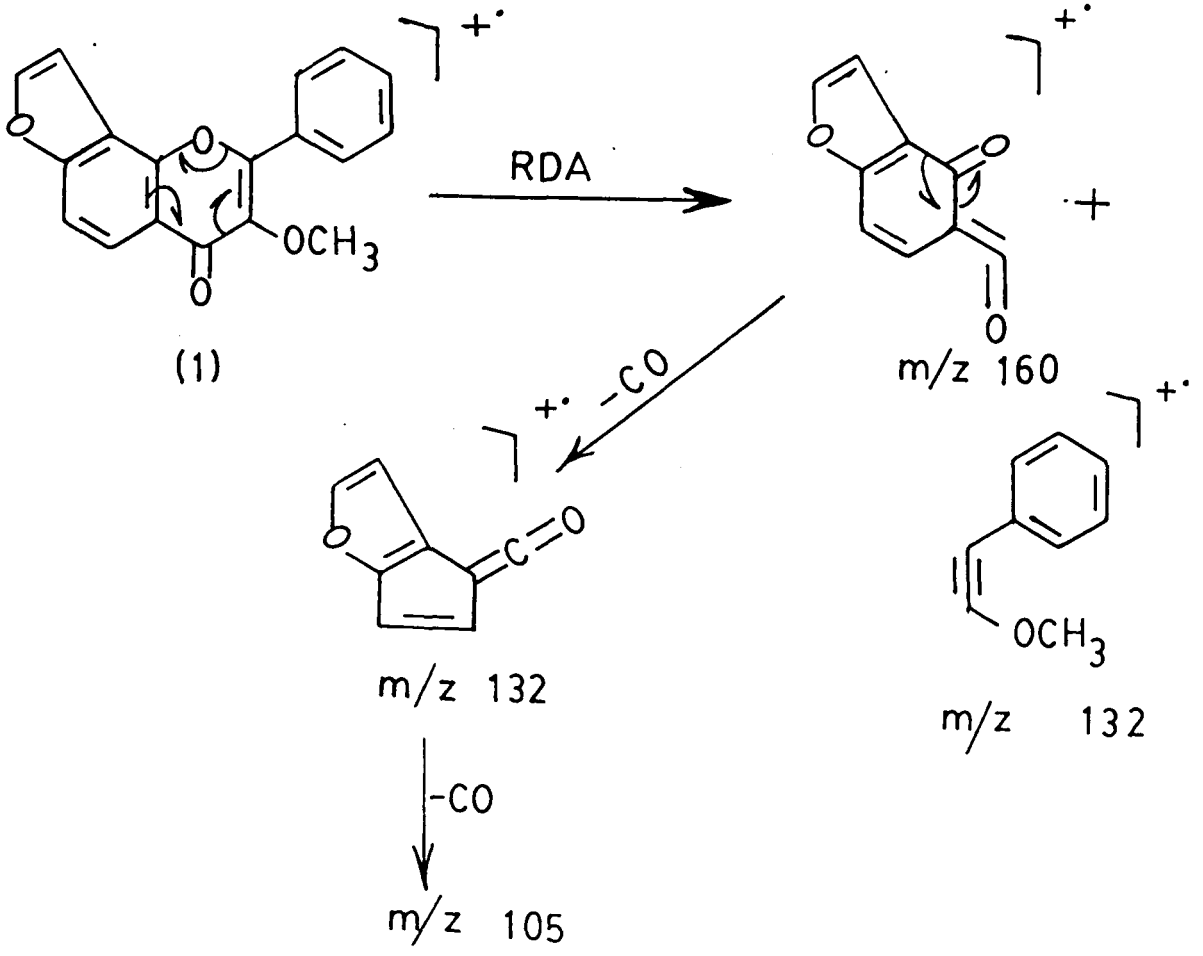
FIG. 3

Reference to literature brought out that loss of hydrogen from the methoxyl group frequently gives rise to strong $M^{+}-1$ peak[13]. The substitution shown in (1) is confirmed by RDA fragments at m/z 160 and 132. The only other prominent peaks in the spectrum arise through loss of CO from $M^{+\bullet}$ and the fragment ions. The mass spectrum can be analysed as shown in Scheme-1. (1) is identical with that of Karanjin[12] which was isolated earlier from Pongamia glabra.




Scheme-1

DS-3 :

Lanceolatin B(2) is a member of the comparatively rare group of furoflavones. The identity of the compound, m.p.138-40°C with lanceolatin B was not initially apparent due to the ambiguous mass spectrum of the compound which indicates $M^{+\bullet}$ at m/z 420. The high mass value suggested a dimeric structure but the low melting point is not compatible with that, so the dimeric structure was ruled out and the peak at 262 a.m.u. was selected as $M^{+\bullet}$. Since this is the mass of lanceolatin B- with which the melting point agreed, further identification was made through direct comparison with the nmr spectrum of the lanceolatin B[14].

The most confusing feature of the nmr spectrum(Fig.4) as far as the identification of this compound is concerned, is the downfield signal at δ6.8 for the C-3 proton. The resonance of this proton usually occurs at δ6.4 and is fairly constant at this value, not usually subjected to any marked dependence on the substitution pattern in the two aromatic rings. Two multiplets integrating for two and four protons fall between δ7.95-7.98 and δ7.50-7.95. The doublet(J=9.16 Hz) of the C-5 proton is discernable at δ8.17 but the doublet of the adjacent C-6 proton is lost in the multiplet centered between δ7.95-7.98. Two other doublets at δ7.22(J=1.83 Hz) and 7.78(J=1.84 Hz) are assigned to the α and β protons of the furan ring.

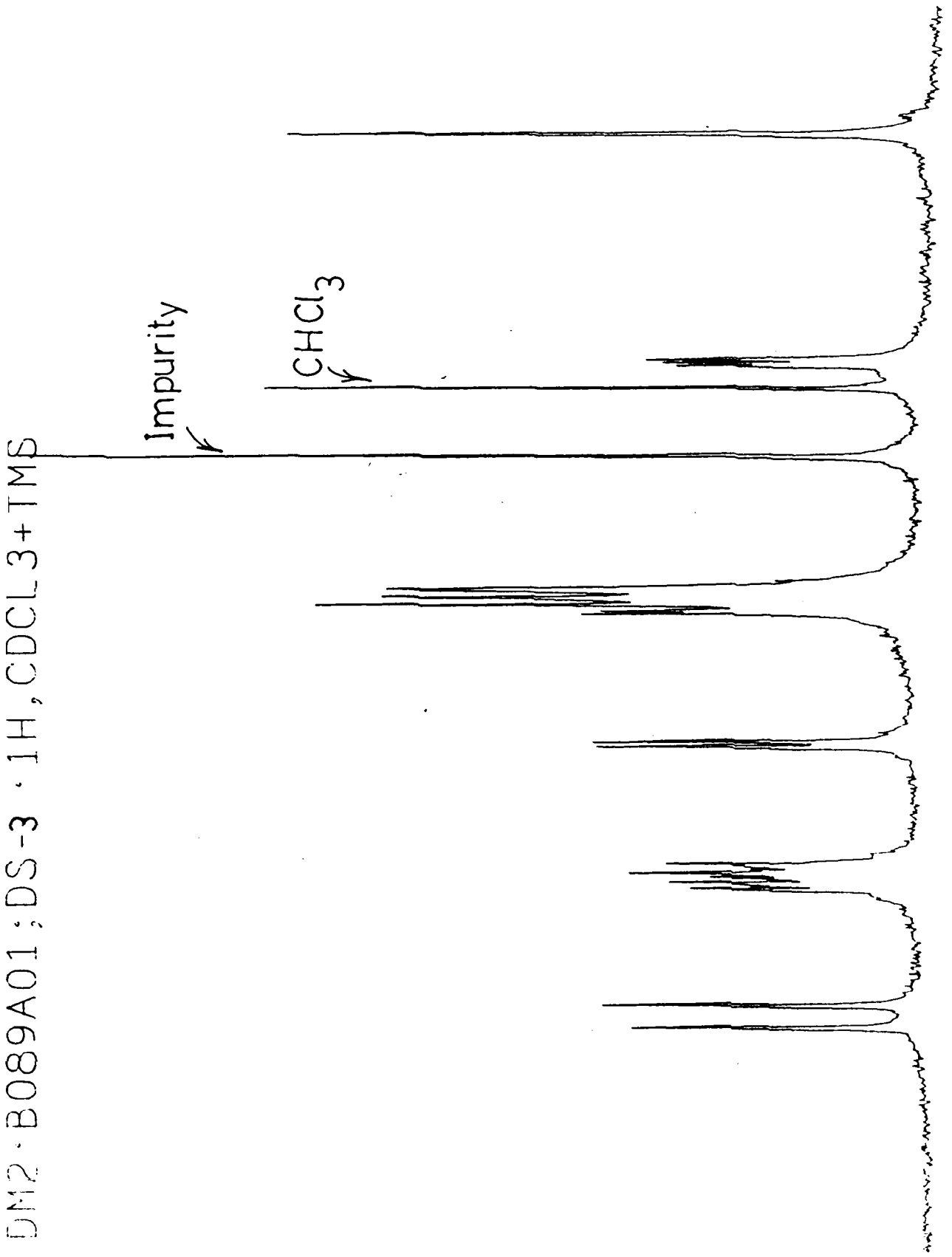

DM2·B089A01;DS-3·1H,CDCL3+TMS
Impurity
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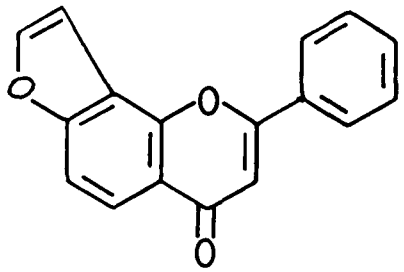
FIG.4



(2)

DS-4 and DS-5

The chloroform extract was chromatographed over silica gel using petrol-chloroform mixture for elution. Concentration of eluates supplied two compounds DS-4 and DS-5 which were crystallized from benzene-petrol. The IR spectra (Fig.5) of both compounds showed carbonyl bands at 1640 and 1625 $cm^{-1}$. DS-4 showed $M^{+\cdot}$ at m/z 336 (Fig.6) and DS-5(Fig.7) at m/z 366 a.m.u. In the nmr spectra the resonances of α and β furanoid protons of a benzofuran moiety are clearly defined. The molecular weights, carbonyl absorption and presence of the benzofuran moiety suggested that both compounds were flavonoid in nature. Singlets at higher field in the nmr spectrum established that DS-4(Fig.8) carried a methylenedioxy and a methoxy group whereas DS-5 (Fig.9) had a methylenedioxy and two methoxy substituents. Since the singlet of the C-3 olefinic hydrogen is missing, the most likely structures for the compounds[15,16] are (3) and (4). The presence of the furan ring can be inferred from the doublet(J=8.5 Hz) of the peri proton which is clearly discernable in the nmr spectra of both compounds. The coupling

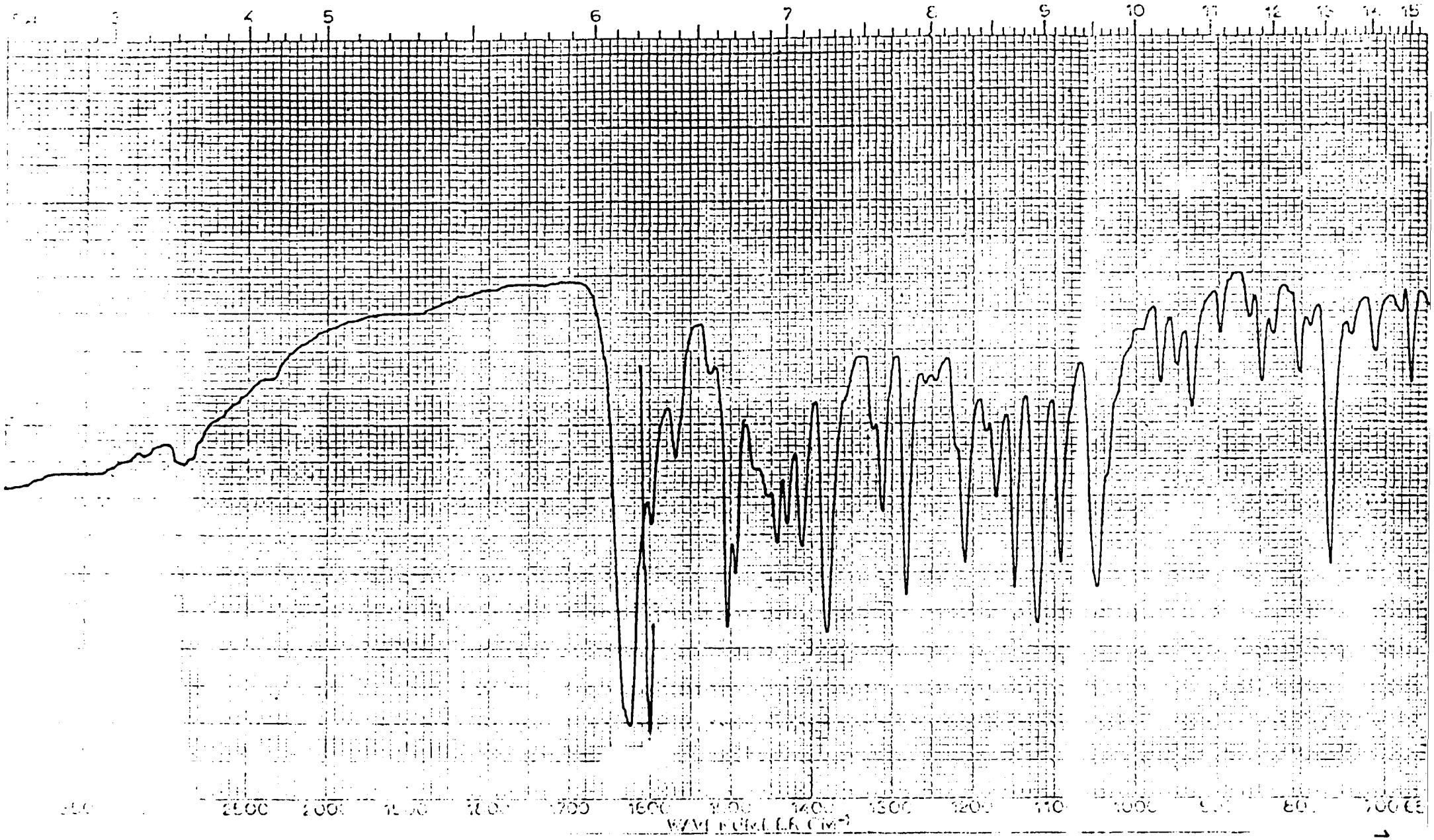

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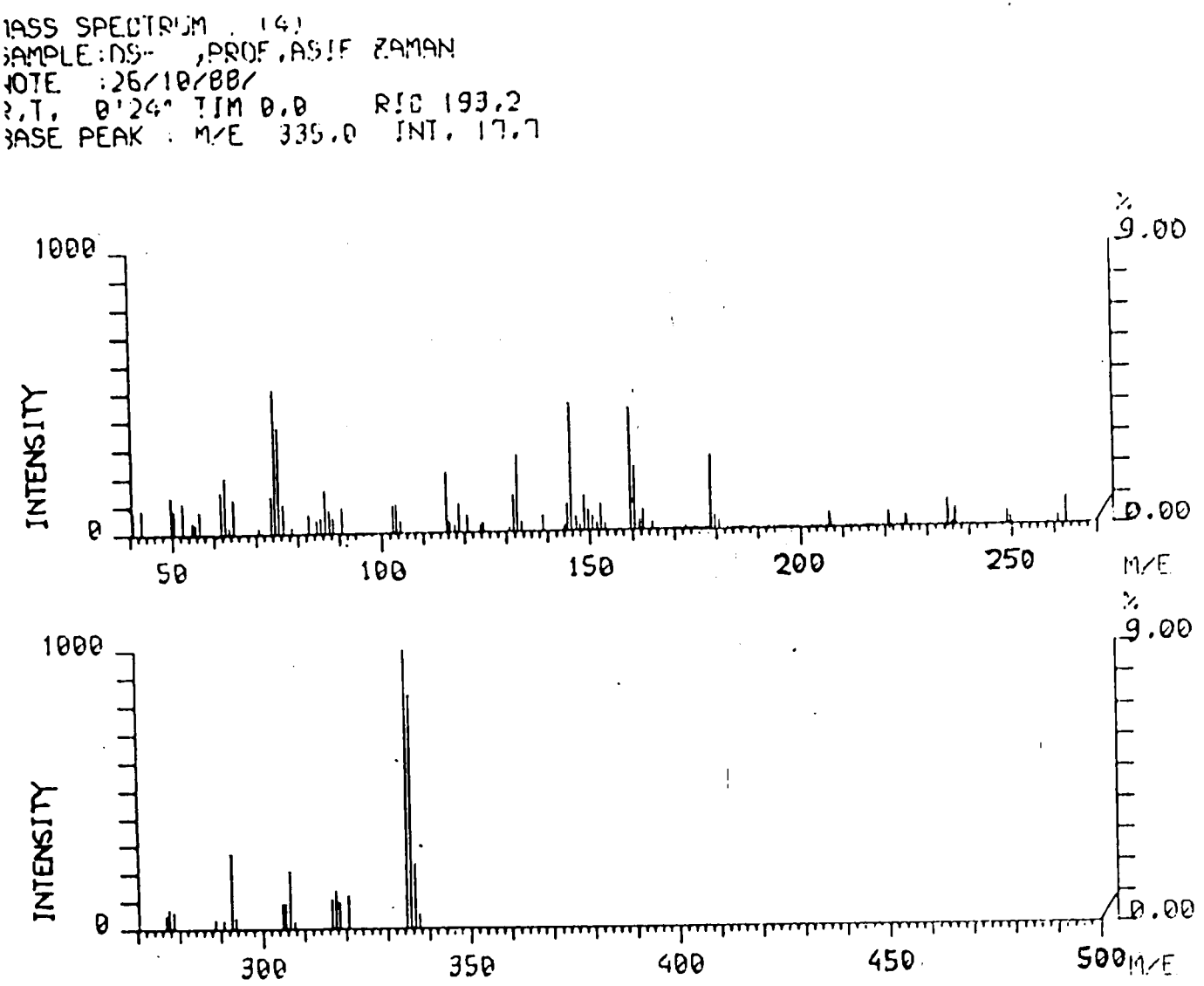
FIG. 5


MASS SPECTRUM . 14)
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BASE PEAK : M/E 335.0 INT. 17.7
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FIG.6

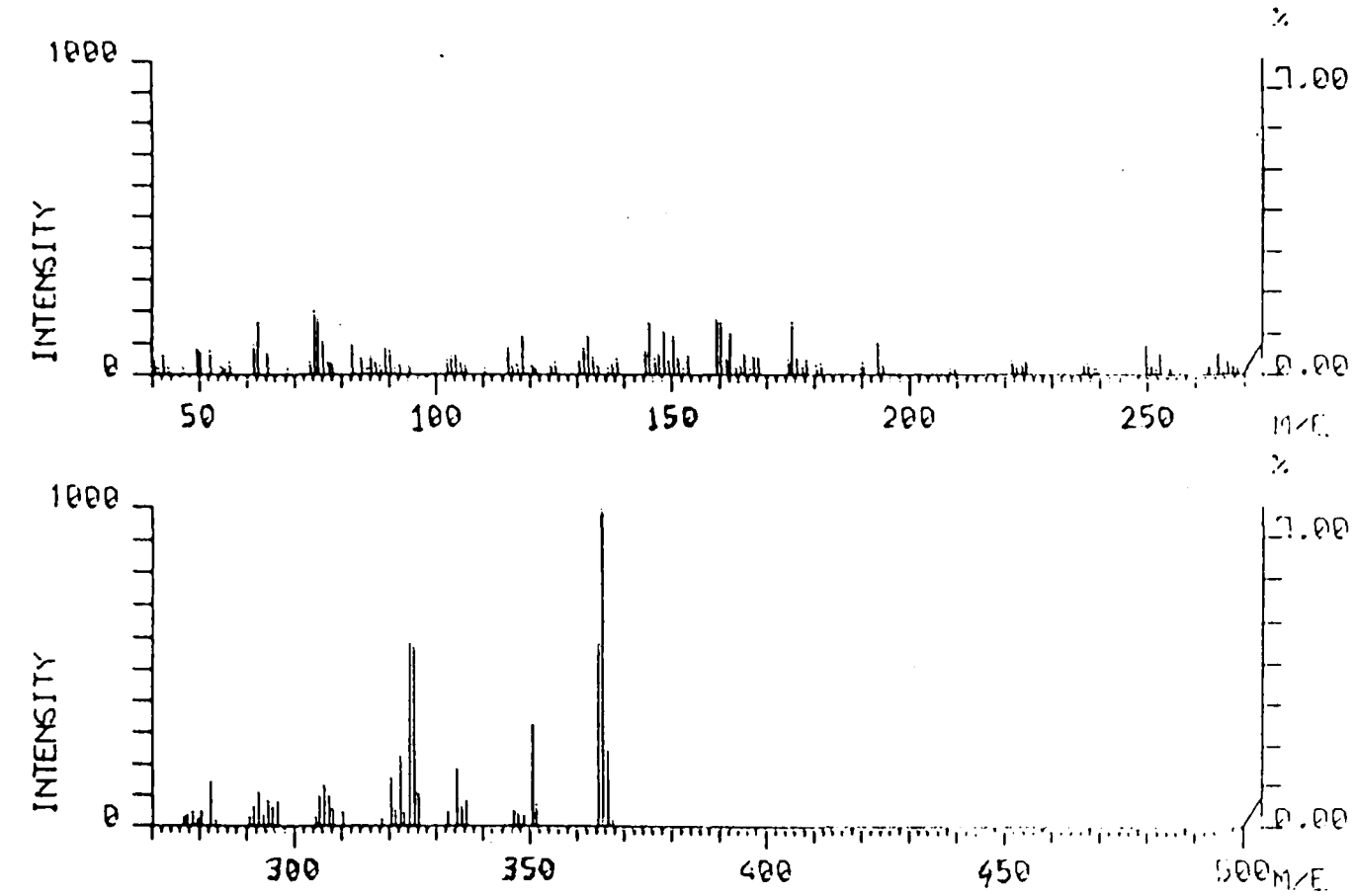
MASS SPECTRUM . 14!
SAMPLE:DS-11,PROF,ASIF ZAMAN
NOTE :26/10/88/
R.T. 0'24" TIM !.0 BIC 2B!.9
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FIG. 7

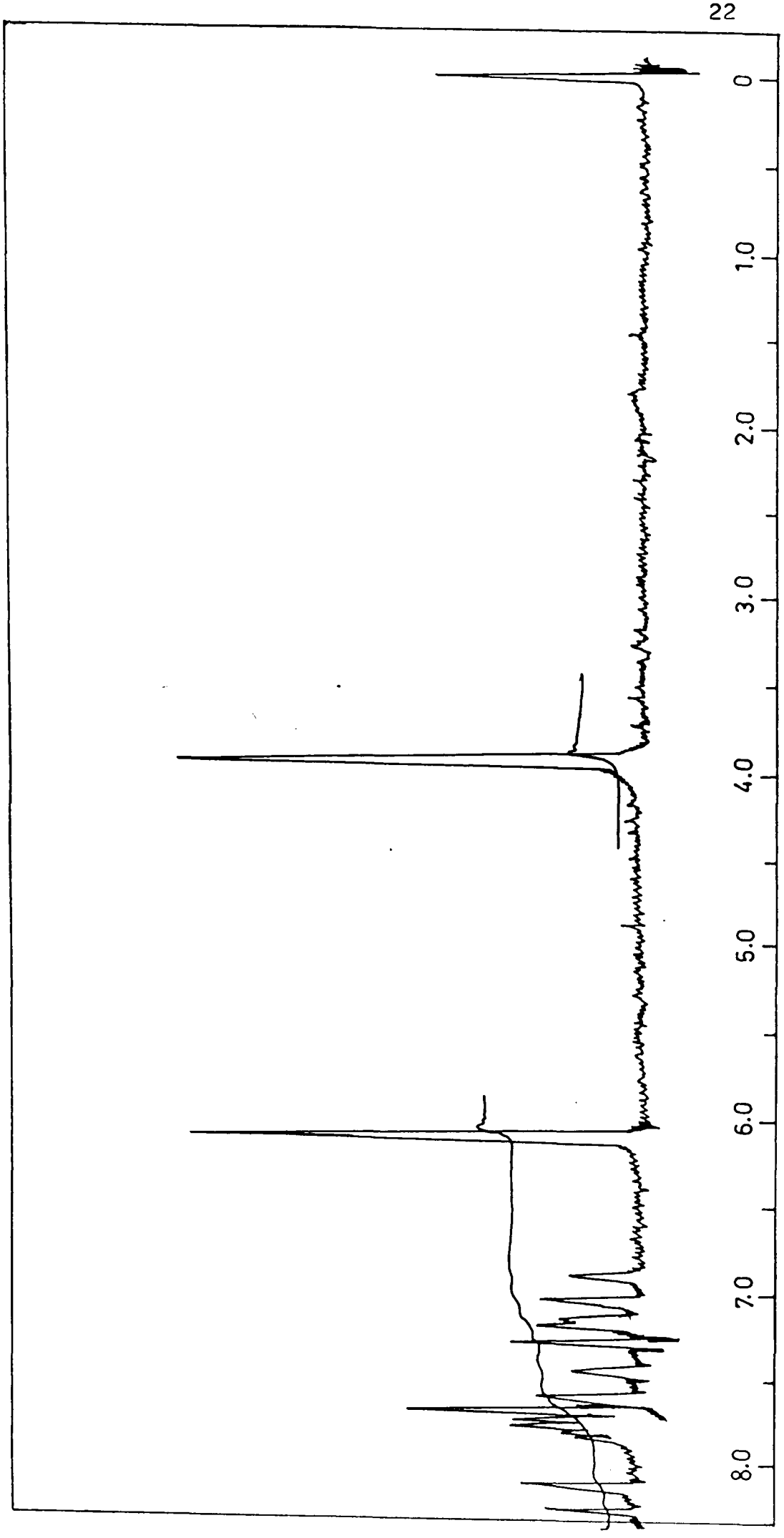



FIG. 8

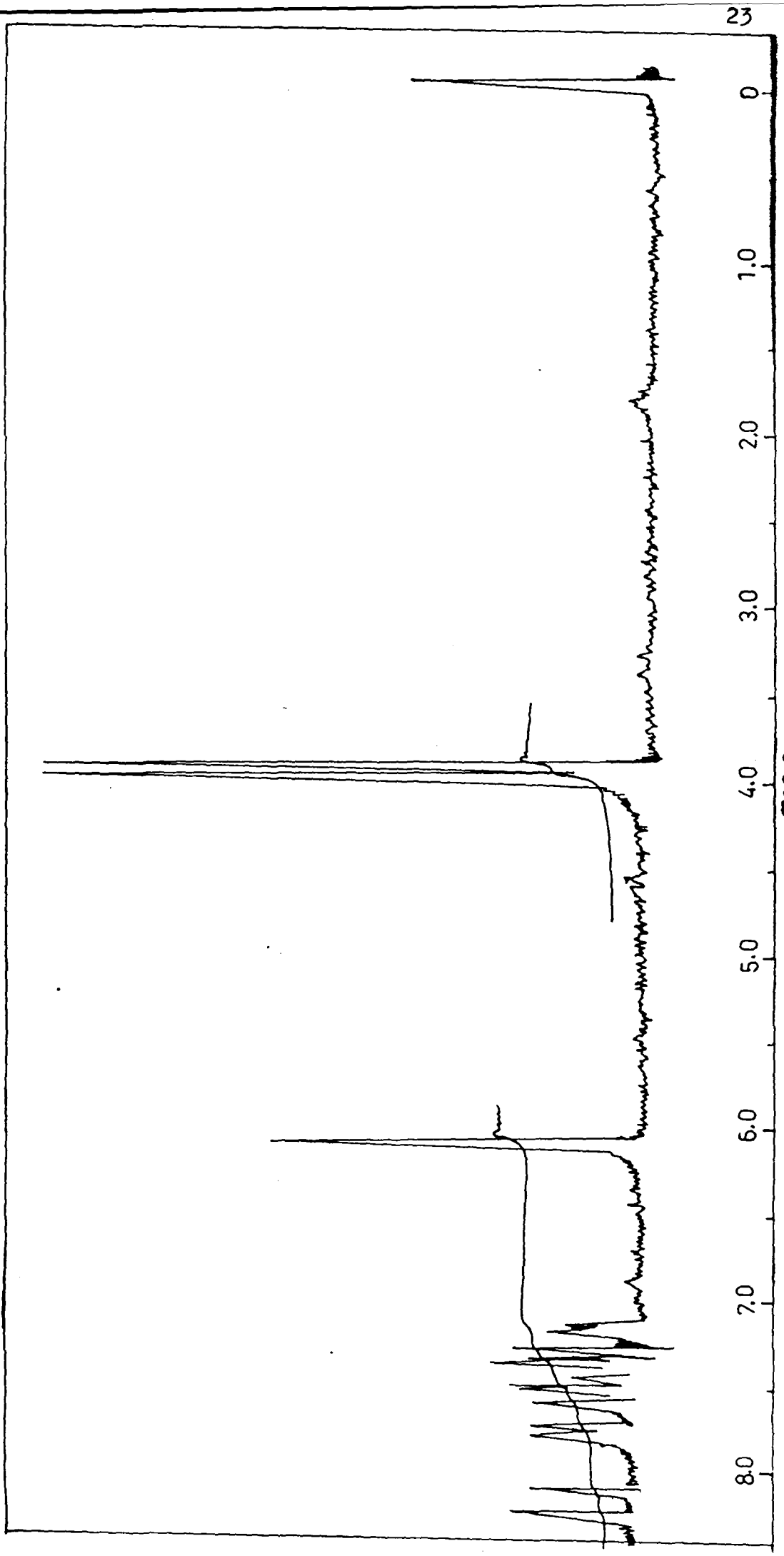
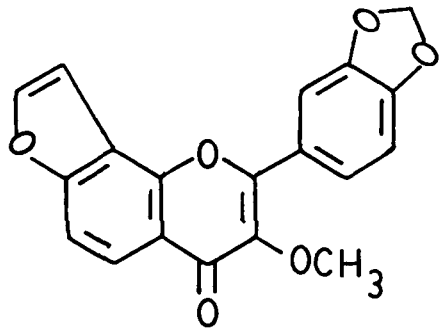
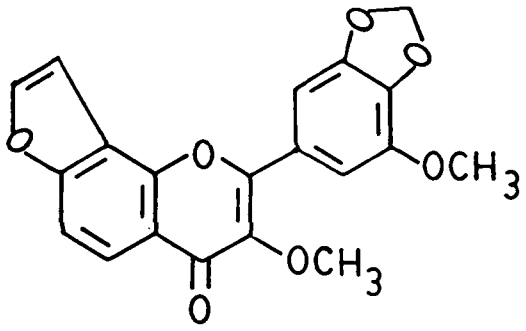



FIG.9

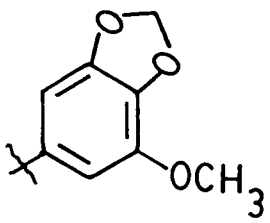


(3)

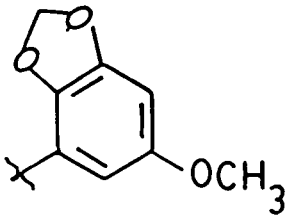


(4)

constant of the other two doublets (J=2 Hz) at δ7.4 and 7.53 in the spectrum of DS-5 establishes that ring B has the substitution shown in (5). The other possibility shown in (6) is unlikely on biogenetic grounds. The fragmentation



(5)

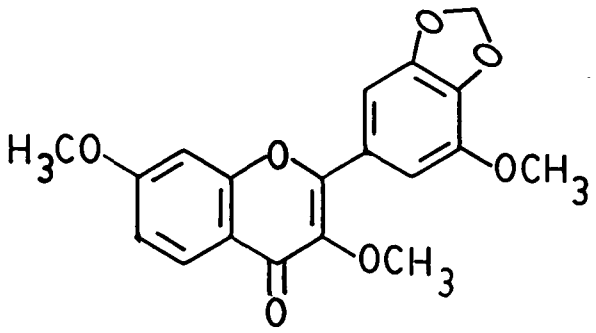


(6)

pattern in the mass spectra further confirms the distribution of substituents in the two rings. Thus the spectra of DS-4 has RDA fragments at m/z 161, 160 and that of DS-5 at m/z 175, 160.

DS-6 :

Elution of the column with chloroform petrol mixture gave a white solid which was crystallized from chloroform/ petrol. Its ir spectrum shows two sharp bands in the carbonyl region, indicating the presence of a chromone moiety in the molecule. The nmr spectrum (Fig.10) reveals three methoxyl methyl singlets between δ3.8-4.0 and one methylenedioxy group at δ6.1. The doublet of the C-5H is clearly indicated at δ8.2 but its counter part appears as double doublet at δ6.9 due to ortho and meta coupling with C-5 and C-8 protons. Since the singlet of the C-3 proton is missing, one arrives at structure(7)[17].




(7)

The third methoxy group is located at the C-5'position as the spectrum shows meta coupled doublets at δ7.32 and 7.44 rather than two 1H singlets which would be the case if the OMe group was at C-6'. Further support for (7) is provided by the mass spectrum(Fig.11) which shows $M^{+\bullet}$ at m/z 356. The RDA fragmentation leads to the fragments at m/z 176 and 150.

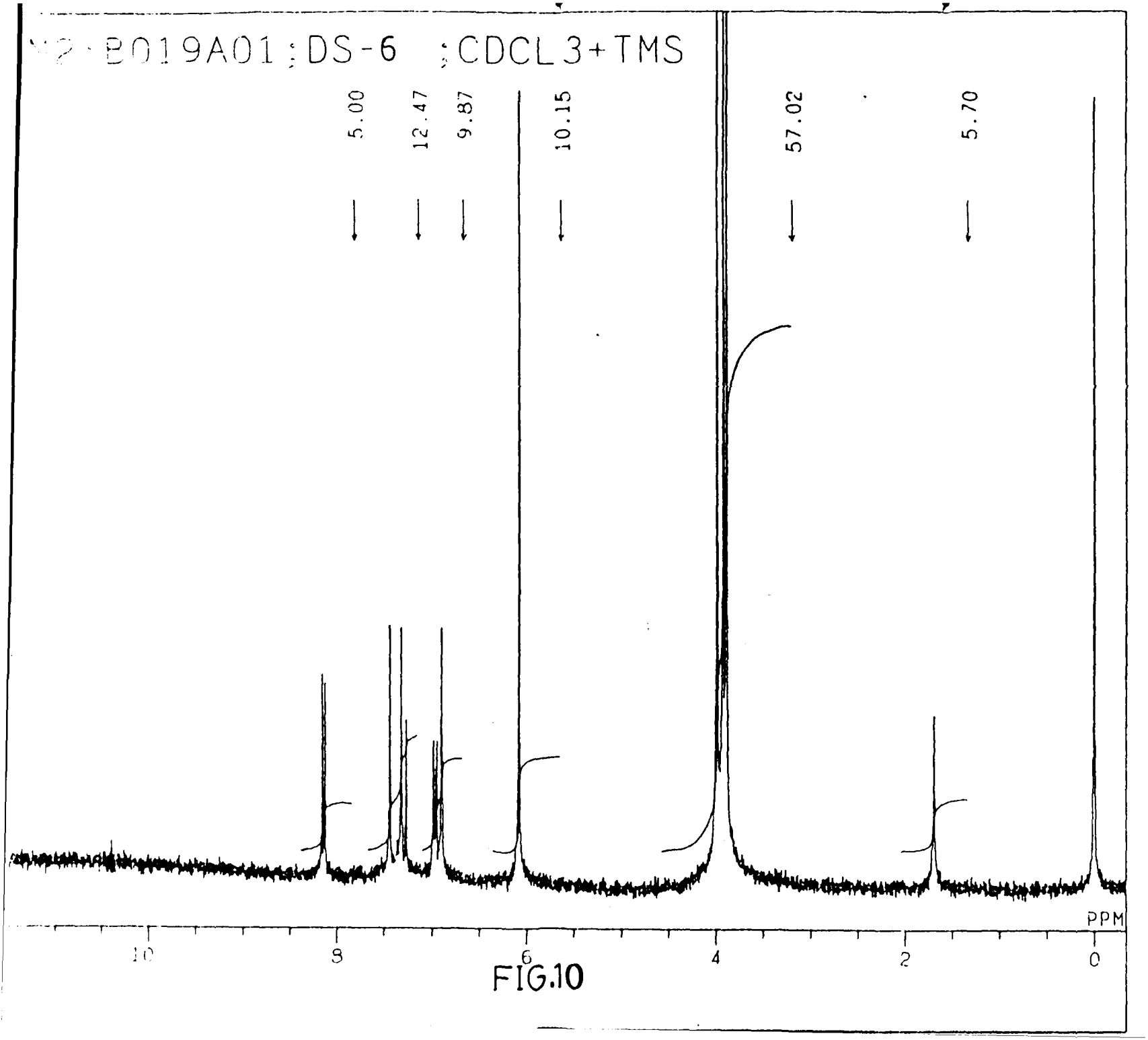



FIG.10

01-FEB-89 10:14:09
DFILE DM2:B019A01
COMNT DM2:B019A01;DS-12
EXMOD SGNON
OBNUC 1H
OBFIN 5930.8 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 12
ACQTM 1.638 sec
PD 2.000 sec
PW1 12.0 us
IRFIN 17600.0 Hz
IRATN 0
TEMP. 35.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 12

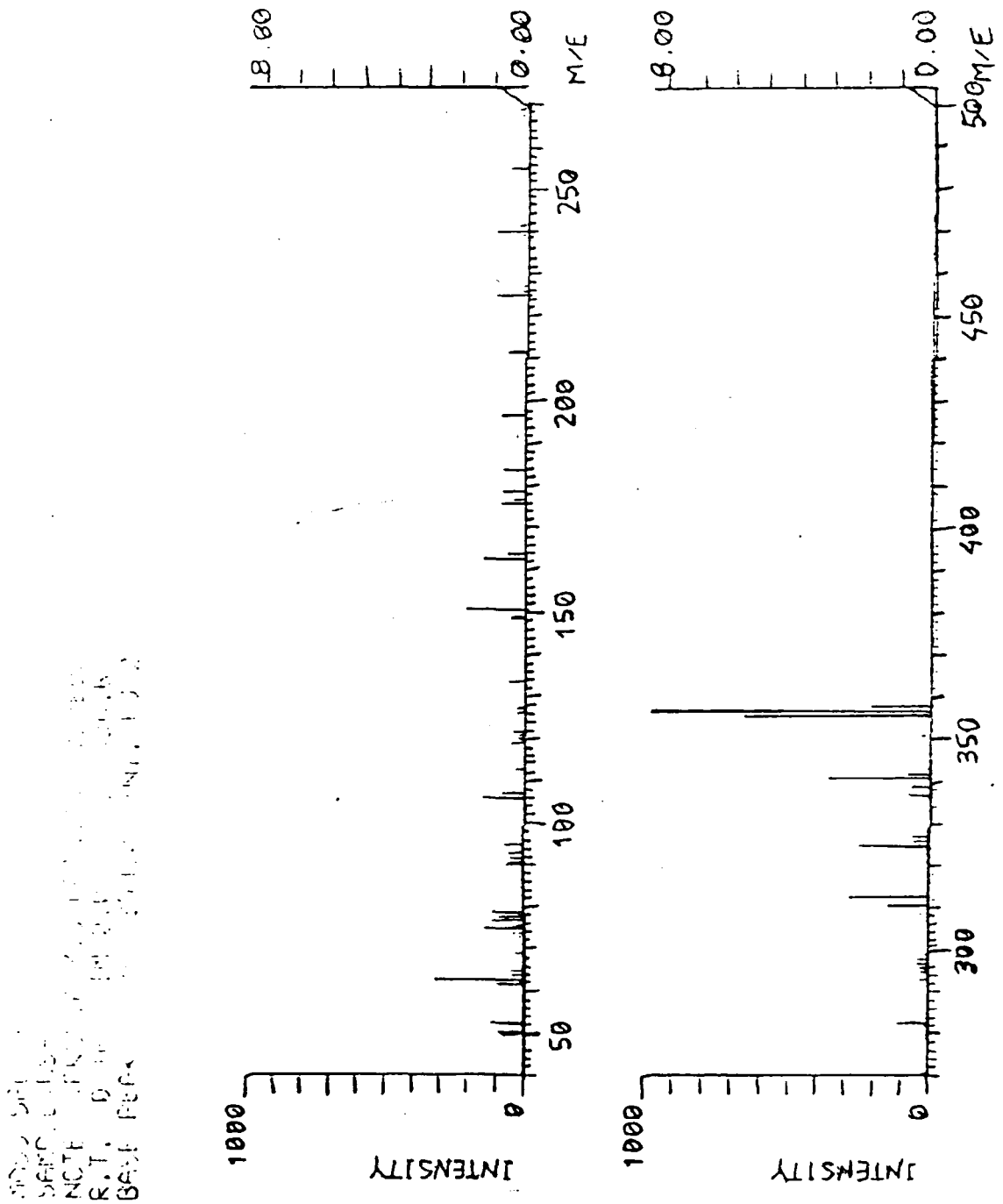
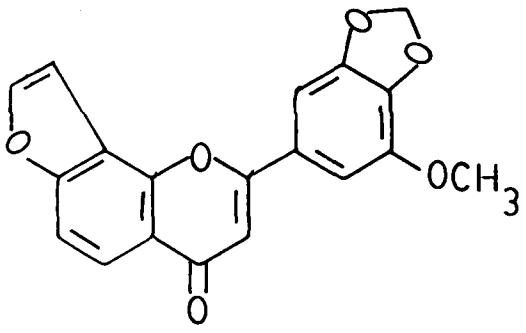

8.00
0.00
M/E
250
200
150
100
50
0
1000
INTENSITY
8.00
0.00
500M/E
450
400
350
300
0
1000
INTENSITY

FIG.11

DS-7 :

Further elution of the column with chloroform-petrol mixture afforded another compound as yellowish brown flakes. The ir spectrum shows a prominent band at 1630 $cm^{-1}$ arising from a chromone moiety in the molecule. The nmr spectrum (Fig.12) offers direct evidence for the flavonoid nature of the compound owing to the presence of the diagnostic singlet of the C-3 olefinic hydrogen. The presence of the benzofuran moiety is inferred from two ortho coupled doublets(J=8.5 Hz) of C-5 and C-6 protons at δ8.2 and 7.5. The singlets at δ4.0 and 6.1 show one methoxy group and one methylenedioxy group in the molecule. The position of the methoxy group at 5' position is established by a sharp singlet integrating for two protons at δ7.15. These facts suggest structure (8) for this compound[18]. Further confirmation for (8) is provided by




(8)

the mass spectrum (Fig.13) indicating $M^{+\bullet}$ at m/z 336. The RDA fragmentation of the molecule leads to the fragment ions at m/z 176 and 160.

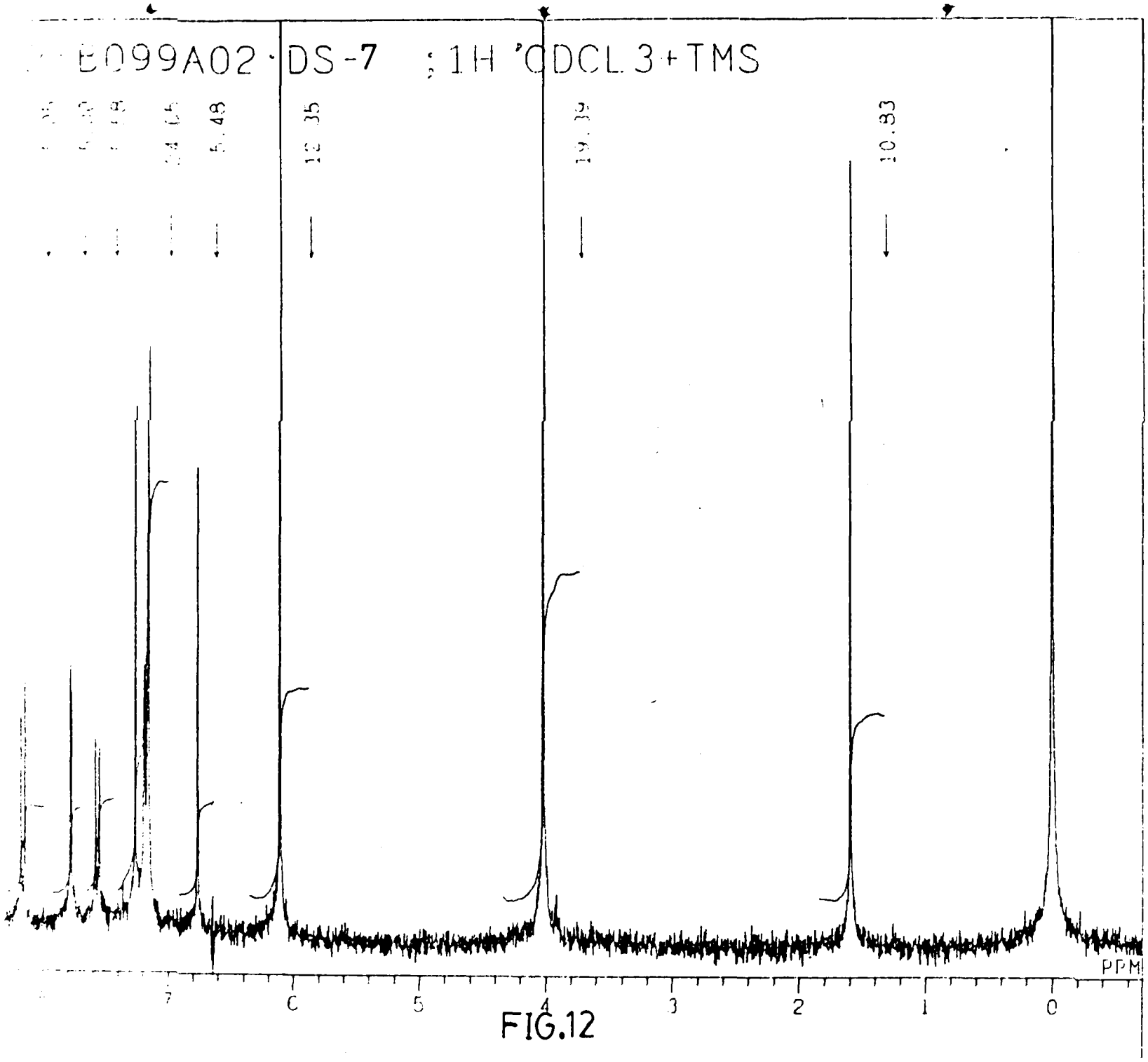



FIG.12

09 FEB 89 15:04:05
DFILE DM2:B099A02
COMNT DM2:B099A02:DS-1
EXMOD SGNON
OBNUC 1H
OBFIN 5400.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 128
ACQTM 1.638 sec
PD 2.000 sec
PW1 10.0 us
IRFIN 17600.0 Hz
IRAT 0
TEM 50.0 c
SLVNT D2O
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 10

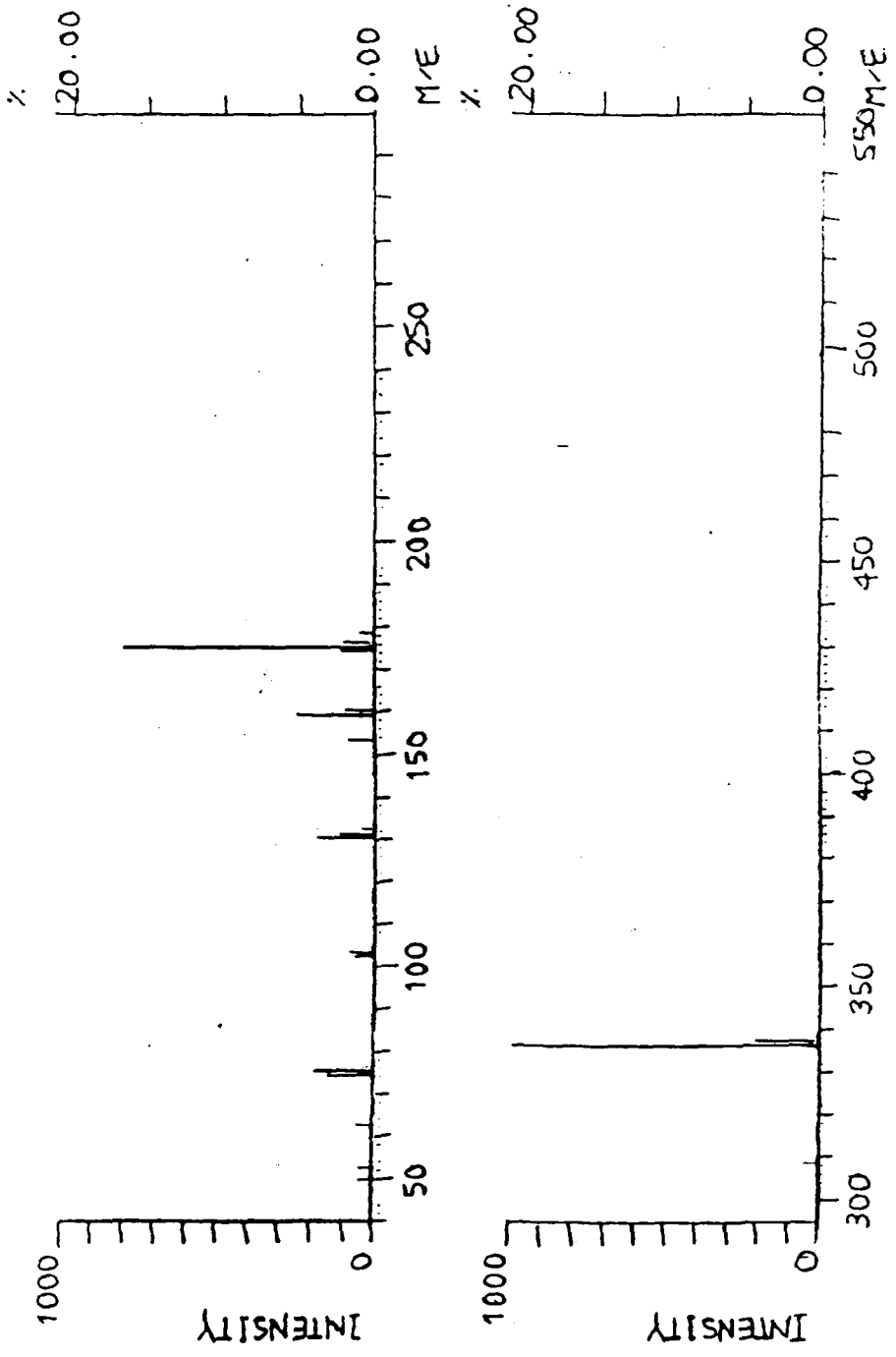

%
20.00
0.00
M/E
INTENSITY
1000
0
50
100
150
200
250
%
20.00
0.00
550M/E
INTENSITY
1000
0
300
350
400
450
500

FIG. 13

# E X P E R I M E N T A L

## EXPERIMENTAL

The melting points are taken on a Kofler block and are uncorrected. Infrared spectra were generally recorded on a SP3-100 PYE UNICAM and IR-408 (Shimadzu) spectrophotometer. Ultravoilet spectra in 95% methanol solutions were measured on a PU 8800 PYE UNICAM spectrophotometer. $^1$H NMR(60 MHz) were recorded at Instrumentation Centre, Department of Chemistry, A.M.U., Aligarh. The 300 MHz NMR and high resolution mass spectra were provided by the Department of Human Biological Chemistry, University of Texas, H.E.J. Research Institute, Karachi and Central Drug Research Institute, Lucknow. The chemical shifts are reported in δ values relative to TMS assigned at zero.

### Desmodium sequax

Extraction:

The stem wood(12 kg) was chopped into small pieces and exhaustively extracted in a soxhlet first with petrol and then with chloroform for 10 days. The petrol extract after removal of the solvent under reduced pressure provided yellowish orange oily mass (18 gm). The residue was chromatographed on a column of silica gel using chloroform-petrol mixture in varying proportions for elution. The compound isolated was labelled as DS-1.

The chloroform extract after removal of the solvent under reduced pressure gave a brownish black gummy residue (40.0 gm). The tlc showed several fluorescent compounds which were also present in the petrol extract. An attempt was made to separate these compounds through preparative tlc but none of them could be isolated owing to their very close RF values. Ultimately the crude material was subjected to the column chromatography using chloroform-petrol mixtures as eluant. The compounds isolated, were labelled as DS-1, DS-3, DS-4, DS-5, DS-6 and DS-7.

DS-1

It was obtained using chloroform-petrol(1:1,v/v) as eluant, crystallized from benzene/petrol to yield transparent white rectangular crystals, 500 mg, m.p.160°C. It was identified as Karanjin through comparison with authentic sample (m.p., ir, nmr and mass).

Spectral Data:

| | |
|---|---|
| UV(MeOH) $\lambda_{max}$ | : 325, 301, 260 and 219 nm. |
| IR(Nujol) $\nu_{max}$ | : 1635, 1625, 1605, 1570, 1525, 1410, 1340, 1285, 1225 and 1160 $cm^{-1}$. |
| $^1H$ NMR(60 MHz) $CDCl_3$ | : $\delta$3.9(3H, s, $-OCH_3$), 7.14(1H, d, -O-CH=CH-), 7.75(1H, d, -O-CH=CH-), 7.4-8.1(6H, m, Ar-H), 8.2(1H, d, J=8.5 Hz). |

Mass (rel.int.) : m/z 292($M^{+\bullet}$,70), 291(100), 273(10), 263(12), 176(5), 160(52), 145(17), 132(20), 105(16), 89(15) and 77(30).

DS-3

Elution of the column with chloroform-petrol(1:1,v/v) gave a fraction which on evaporation yielded an orange yellow mass(4.0 g). The residue was further chromatographed over silica gel using benzene-ethylacetate(98:2) as eluant. Appropriate fractions were combined and evaporated to give a solid which on crystallisation from benzene yielded cream coloured needles(75 mg), m.p.138-40°C.

Spectral Data:

UV(MeOH) $\lambda_{max}$ : 370, 292, 260 and 215 nm.

IR(KBr) $\nu_{max}$ : 1655, 1620, 1585, 1540, 1462, 1420, 1375, 1270, 1152, 1080 and 862 $cm^{-1}$.

$^1H$ NMR(300 MHz) $CDCl_3$ : δ6.89(1H, s, C-3), 7.22(1H, d, -O-CH=C<u>H</u>-, J=1.84 Hz), 7.78(1H, d, -O-C<u>H</u>=CH-, J=1.83 Hz), 7.55-7.59 (4H, m, Ar-<u>H</u>), 7.95-7.99(2H, m, Ar-<u>H</u>), 8.17(1H, d, C-5, J=9.16 Hz).

Mass(rel.int.) : m/z 262($M^{+\bullet}$, 100), 234(100), 205(14), 176(24), 161(100), 160(100), 132 (100), 117(80), 105(25), 104(86), 102(49) and 77(46).

The compound was identified as lanceolatin B on comparison (m.m.p., nmr and mass) with an authentic sample.

DS-4

It was obtained from a mixture of chloroform-petrol (1:1, v/v), crystallized from benzene/petrol to yield off-white granules (100 mg), m.p. 192-200°C. It was characterised as pongapin through direct comparison (Co tlc, m.p., ir, nmr and mass) with an authentic sample.

Spectral Data:

UV(MeOH) $\lambda_{max}$ : 370, 340, 315, 245 and 212 nm.

IR(KBr) $\nu_{max}$ : 1640, 1625, 1600, 1570, 1500, 1450, 1415, 1375, 1330, 1290, 1260, 1215, 1045 and 760 $cm^{-1}$.

$^1H$ NMR(60 MHz) $CDCl_3$ : δ3.90(3H, s, O-C<u>H</u>$_3$), 6.1(2H, s, -O-C<u>H</u>$_2$-O), 7.20(1H, d, -O-C<u>H</u>=C<u>H</u>-, J=2Hz), 7.75(1H, d, -O-C<u>H</u>=CH-, J=2Hz), 7.0(1H, d, C-5', J=8.5 Hz), 7.67-7.85(2H, m, C-2' and C-6'), 7.5(1H, d, C-6, J=8.5 Hz), 8.2(1H, d, C-5, J=8.5 Hz).

Mass(rel.int.) : m/z 336($M^{+\bullet}$, 84), 335(100), 321(12), 318(14), 307(21), 293(27), 161(25), 160(44), 146(48) and 77(32).

DS-5

It was also eluted with chloroform-petrol(1:1, v/v), crystallized from benzene/petrol to afford white granules(150 mg), m.p.178-80°C, characterized as methoxy pongapin through direct comparison with spectral data.

Spectral Data:

| | |
|---|---|
| UV(MeOH) $\lambda_{max}$ | : 370, 340, 318, 244 and 216 nm |
| IR(KBr) $\nu_{max}$ | : 1625, 1600, 1570, 1525, 1505, 1495, 1445, 1415, 1380, 1315, 1285, 1040, 1020 and 765 $cm^{-1}$. |
| $^1H$ NMR(60 MHz) $CDCl_3$ | : δ3.9(3H, s, $OC\underline{H}_3$), 4.0(3H, s, $-OC\underline{H}_3$), 6.10(2H, s, $-O-C\underline{H}_2-O-$), 7.18(1H, d, $-O-CH=C\underline{H}-$, J=2Hz), 7.78(1H, d, $-O-C\underline{H}=CH-$, J=2Hz), 7.38(1H, d, C-2'), 7.54(1H, d, C-6'), 7.50(1H, d, C-6, J=8Hz), 8.2(1H, d, C-5, J=8Hz). |
| Mass(rel.int.) | : m/z 366($M^{+\cdot}$, 100), 365(58), 351(33), 326(57), 325(58), 175(16), 160(17) and 77(5). |

DS-6

It was obtained from chloroform-petrol(3:2) eluates, crystallized from benzene/petrol as white feathry solid(100 mg),

m.p. 204-206 °C, soluble in chloroform on slight heating, identified as Kanujin.

Spectral Data:

UV(MeOH) $\lambda_{max}$ : 370, 340, 313 and 216 nm.

IR(KBr) $\nu_{max}$ : 1640, 1620, 1505, 1450, 1395, 1260, 1210, 1130, 1055, 1015 and 830 $cm^{-1}$.

$^1H$ NMR(300 MHz) $CDCl_3$ : δ3.88(3H, s, -O-C<u>H</u>$_3$), 3.92(3H, s, -O-C<u>H</u>$_3$), 3.98(3H, s, -O-C<u>H</u>$_3$), 6.07 (2H, s, -O-C<u>H</u>$_2$-O-), 8.16(1H, d, C-5), 6.95(1H, dd, C-6), 6.88(1H, d, C-8), 7.30(1H, d, C-2'), 7.44(1H, d, C-6').

Mass(rel.int.) : m/z 356($M^{+\cdot}$, 67), 341(37), 325(24), 311(15), 176(5), 162(7), 150(20) and 63(30).

DS-7

It was obtained from a mixture of chloroform and petrol(2:1, v/v), cyrstallized from benzene to yield brownish yellow flakes(62 mg), m.p.256-60°C, identified as glabra-II.

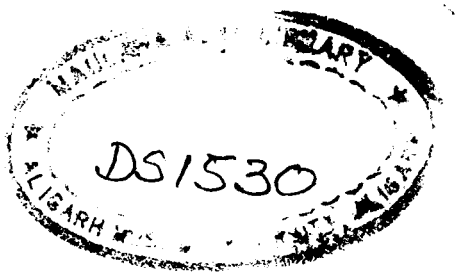
Spectral Data:

UV(MeOH) $\lambda_{max}$ : 370, 340, 317, 240 and 221 nm.

IR(KBr) $\nu_{max}$ : 1630, 1585, 1505, 1452, 1435, 1400, 1380, 1352, 1325, 1215, 1172, 1100 and 1045 $cm^{-1}$.

$^1H$ NMR(300 MHz) $CDCl_3$ : $\delta$4.0(3H, s, O-C<u>H</u>$_3$), 6.10(2H, s, -O-C<u>H</u>$_2$-O), 6.76(1H, s, C-3), 7.18 (1H, d, -O-CH=C<u>H</u>-), 7.75(1H, d, -O-C<u>H</u>=CH-), 7.15(2H, s, C-2', 6'), 7.54(1H, d, C-6, J=9.16 Hz), 8.2 (1H, d, C-5, J=8.54 Hz).

Mass(rel.int.) : m/z 336 ($M^{+\bullet}$, 100), 176(80), 160 (24), 131(13) and 77(14).



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